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DESCRIPTION

Method of Manufacturing Oxide Superconducting Wire, Method of Modifying Oxide Superconducting Wire and Oxide Superconducting Wire

5 Technical Field

The present invention relates to a method of manufacturing an oxide superconducting wire, a method of modifying an oxide superconducting wire and an oxide superconducting wire, and more particularly, it relates to a method of manufacturing an oxide superconducting wire capable of improving the critical current
10 density, a method of modifying an oxide superconducting wire and an oxide superconducting wire.

Background Art

In general, a method of obtaining an oxide superconducting wire by heat-treating a wire formed by charging a metal tube with raw material powder of an oxide
15 superconductor and thereafter wiredrawing and rolling the metal tube for sintering the raw material powder of the oxide superconductor is known as a method of manufacturing an oxide superconducting wire. However, the wire is blistered in the aforementioned heat treatment step for sintering, to disadvantageously reduce the superconductivity of the obtained oxide superconducting wire.

20 Japanese Patent Laying-Open No. 5-101723 (Patent Document 1) proposes a method of manufacturing an oxide superconducting wire by heat-treating a metal tube filled with powder of an oxide superconductor or a flattened body thereof in a pressurized atmosphere for sintering the powder of the oxide superconductor. The aforementioned gazette describes that a wire having excellent superconductivity is
25 obtained according to this method by performing a pressure heat treatment.

More specifically, it is attempted to store a metal tube charged with powder of an oxide superconductor in a heat-resistant/pressure-resistant closed vessel for preventing blistering in sintering by increasing the internal pressure following heat-up in

the closed vessel. The aforementioned gazette describes that the current internal pressure can be obtained from a state equation of gas or the like, and an internal pressure of about 4 atm. can be obtained with a heating temperature of about 900°C, for example.

5 Japanese Patent No. 2592846 (Japanese Patent Laying-Open No. 1-30114) (Patent Document 2) proposes a method of manufacturing an oxide superconducting conductor by holding a metal tube filled with oxide superconducting powder or the like in a high-pressure state at least either in a heat treatment or after the heat treatment. The aforementioned gazette describes that partial separation on the interface between
10 the oxide superconductor and the metal tube caused in sintering can be prevented according to this method by setting the metal tube in the high-pressure state.

More specifically, the metal tube filled with the oxide superconducting powder can be press-fitted to a sintered body by holding the metal tube in a high-pressure state of 500 to 2000 kg/cm² (about 50 to 200 MPa) at least either in the heat treatment or
15 after the heat treatment. Thus, when the superconductor partially causes quenching, heat resulting from this quenching can be quickly removed. In addition, it is also possible to prevent deterioration of the superconductivity resulting from a separation part forming a stress concentration part causing distortion.

Patent Document 1: Japanese Patent Laying-Open No. 5-101723

20 Patent Document 2: Japanese Patent No. 2592846 (Japanese Patent Laying-Open No. 1-30114)

Disclosure of the Invention

Problems to be Solved by the Invention

In Japanese Patent Laying-Open No. 5-101723, however, the internal pressure
25 obtained following heat-up in the closed vessel is about 4 atm (0.4 MPa). Thus, voids are formed between oxide superconducting crystals in sintering, to disadvantageously reduce the critical current density.

Further, the oxide superconducting wire cannot be sufficiently inhibited from

blistering caused in sintering due to the internal pressure of about 4 atm (0.4 MPa), and hence the critical current density is also disadvantageously reduced.

In the method according to Japanese Patent No. 2592846, it is difficult to control the partial oxygen pressure in the heat treatment due to application of the
5 excessively high pressure of 500 to 2000 kg/cm² (about 50 MPa to 200 MPa), to reduce the critical current density.

Accordingly, an object of the present invention is to provide a method of manufacturing an oxide superconducting wire capable of improving the critical current density by suppressing formation of voids between oxide superconducting crystals and
10 blisters of the oxide superconducting wire while simplifying partial oxygen pressure control in a heat treatment, a method of modifying an oxide superconducting wire and an oxide superconducting wire.

Means for Solving the Problems

The method of manufacturing an oxide superconducting wire according to the
15 present invention comprises a step of preparing a wire formed by covering raw material powder of an oxide superconductor with a metal and a heat treatment step of heat-treating the wire in a pressurized atmosphere having a total pressure of at least 1 MPa and less than 50 MPa in the heat treatment. At a heat-up time before the heat treatment in the heat treatment step, pressurization is started from a temperature
20 reducing 0.2 % yield strength of the metal below the total pressure in the heat treatment.

The method of modifying an oxide superconducting wire according to the present invention comprises a heat treatment step of heat-treating an oxide superconducting wire formed by covering an oxide superconductor with a metal in a pressurized atmosphere having a total pressure of at least 1 MPa and less than 50 MPa
25 in the heat treatment. At a heat-up time before the heat treatment in the heat treatment step, pressurization is started from a temperature reducing 0.2 % yield strength of the metal below the total pressure.

According to the inventive method of manufacturing or modifying an oxide

superconducting wire, a pressure is applied to the wire in a state where the 0.2 % yield strength of the metal is smaller than the total pressure of the pressurized atmosphere in the heat treatment. Thus, the portion of the metal is readily compressed through compressive force resulting from pressurization due to an effect similar to that of hot
5 working. Therefore, the wire is compressed before pressurizing gas penetrates into the wire through pinholes, whereby formation of voids and blisters can be sufficiently suppressed by the pressurization. Consequently, the sintering density of the oxide superconductor can be improved, and the critical current density of the oxide superconducting wire can be improved.

10 Another method of manufacturing an oxide superconducting wire according to the present invention comprises a step of preparing a wire formed by covering raw material powder of an oxide superconductor with a metal including silver and a heat treatment step of heat-treating the wire in a pressurized atmosphere having a total pressure of at least 1 MPa and less than 50 MPa in the heat treatment. At a heat-up time before the
15 heat treatment in the heat treatment step, pressurization is started after the temperature of the atmosphere exceeds 400°C.

Another method of modifying an oxide superconducting wire according to the present invention comprises a heat treatment step of heat-treating an oxide superconducting wire formed by covering an oxide superconductor with a metal
20 including silver in a pressurized atmosphere having a total pressure of at least 1 MPa and less than 50 MPa in the heat treatment. At a heat-up time before the heat treatment in the heat treatment step, pressurization is started after the temperature of the atmosphere exceeds 400°C.

According to this inventive method of manufacturing or modifying an oxide
25 superconducting wire, a pressure is applied to the wire in a state where 0.2 % yield strength of the metal including silver is reduced to a level substantially identical to the total pressure of the pressurized atmosphere in the heat treatment. Thus, the portion of the metal is readily compressed through compressive force resulting from pressurization

due to an effect similar to that of hot working. Therefore, the wire is compressed before pressurizing gas penetrates into the wire through pinholes, whereby formation of voids and blisters can be sufficiently suppressed by the pressurization. Consequently, the sintering density of the oxide superconductor can be improved, and the critical current density of the oxide superconducting wire can be improved.

Preferably in the aforementioned manufacturing and modifying methods, the pressurization is started after the temperature of the atmosphere exceeds 600°C at the heat-up time before the heat treatment in the heat treatment step.

Thus, the pressure is applied to the wire in a state where the 0.2 % yield strength of the metal including silver is reduced to about half the total pressure of the pressurized atmosphere in the heat treatment. Therefore, the portion of the metal is further readily compressed through the compressive force resulting from the pressurization. Consequently, the sintering density of the oxide superconductor can be further improved, and the critical current density of the oxide superconducting wire can be further improved.

Preferably in the aforementioned manufacturing and modifying methods, the speed of pressurization is at least 0.05 MPa/min.

The inventors have found that the speed of the pressurizing gas penetrating into the wire through pinholes is less than about 0.05 MPa/min. in the heat treatment step.

When the total pressure of the atmosphere is controlled to continuously increase at a speed of at least 0.05 MPa/min. at the heat-up time before the heat treatment, therefore, the pressure in the atmosphere can be regularly kept higher than the pressure in the wire. Thus, compressive force can be applied to the wire at the heat-up time before the heat treatment whether or not the wire has pinholes before the heat treatment step, whereby formation of voids and blisters is suppressed. Consequently, the sintering density of the oxide superconductor can be effectively improved due to the heat treatment in the pressurized atmosphere of at least 1 MPa and less than 50 MPa, and the critical current density of the oxide superconducting wire can be effectively improved.

Preferably in the aforementioned manufacturing and modifying methods, the speed of pressurization is at least 0.1 MPa/min.

Thus, the pressure in the atmosphere can be kept further higher than the pressure in the wire. Therefore, the compressive force can be further largely applied to the wire at the heat-up time before the heat treatment whether or not the wire has pinholes before the heat treatment step, whereby formation of voids and blisters is suppressed.

Consequently, the sintering density of the oxide superconductor can be further effectively improved due to the heat treatment in the pressurized atmosphere of at least 1 MPa and less than 50 MPa, and the critical current density of the oxide superconducting wire can be further effectively improved.

Preferably in the aforementioned manufacturing and modifying methods, the heat treatment step is carried out in an oxygen atmosphere, and the partial oxygen pressure is at least 0.003 MPa and not more than 0.02 MPa.

When the partial oxygen pressure is kept in the range of at least 0.003 MPa and not more than 0.02 MPa in the heat treatment, a stable oxide superconducting phase is formed and the critical current density can be improved. A non-superconducting phase is formed if the partial oxygen pressure exceeds 0.02 MPa, while the oxide superconducting phase is hardly formed and the critical current density is reduced if the partial oxygen pressure is less than 0.003 MPa.

Preferably in the aforementioned manufacturing method, the raw material powder of the oxide superconductor includes a Bi2223 phase, and the oxide superconducting wire is annealed in an oxygen-containing atmosphere of a temperature of at least 300°C and not more than 600°C in the heat treatment step.

Preferably in the aforementioned modifying method, the oxide superconducting wire includes a Bi2223 phase, and the oxide superconducting wire is annealed in an oxygen-containing atmosphere of a temperature of at least 300°C and not more than 600°C in the heat treatment step.

The inventors have noted that a Bi2212 phase is included in an oxide

superconductor mainly composed of a Bi2223 phase and have made deep studies to find that the oxygen content of the Bi2212 phase changes when the oxide superconductor is annealed in an oxygen atmosphere to improve the critical current density at a low temperature of about 20 K. The principle of the improvement of the critical current density at the low temperature of about 20 K is now described.

An oxide superconductor (oxide superconductor filaments) of an oxide superconducting wire includes a Bi2212 phase in addition to a main phase of a Bi2223 phase (no wire of an oxide superconductor consisting of a 2223 phase by 100 % is implemented at present). When this wire is annealed in an oxygen atmosphere so that the Bi2212 phase absorbs oxygen, low-temperature characteristics of the wire are improved due to the following properties:

(1) As to Bi2212 Phase

In the Bi2212 phase, the oxygen content remarkably changes when the wire is annealed in an oxygen atmosphere. In other words, a value z in $(\text{BiPb})_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+z}$ changes due to the annealing in the oxygen atmosphere, to change the critical temperature (T_c) and the critical current density (J_c) of the Bi2212 phase. More specifically, the critical temperature T_c is reduced (changes in the range of 70 K to 90 K) when the value z is increased. Further, the critical current density J_c is increased at a low temperature of about 20 K, while the critical current density J_c is reduced at a high temperature of about 77 K.

This change is caused since the concentration of carriers (holes) bearing conduction is increased when the oxygen content in the Bi2212 phase is increased. In other words, the critical temperature T_c is reduced if oxygen is excessively introduced since there is an optimum hole concentration increasing T_c in relation to the critical temperature T_c , while the critical current density J_c is improved since electrical conduction is improved as the carrier concentration is increased in relation to the critical current density J_c at a temperature sufficiently lower than the critical temperature T_c . In relation to the critical current density J_c at a high temperature, the critical temperature

T_c (77 K, for example: since the critical temperature T_c of the Bi2212 phase is close to or not more than the same) is reduced and hence the critical current density J_c is also reduced.

(2) As to Bi2223 Phase

The Bi2223 phase extremely hardly absorbs or discharges oxygen, and the oxygen content thereof hardly changes when the wire is annealed in the oxygen atmosphere. In other words, the value z in $(\text{BiPb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+z}$ substantially remains at zero. Therefore, the critical temperature T_c and the critical current density J_c of the Bi2223 phase remain unchanged when the wire is annealed in the oxygen atmosphere.

As understood from Table 1 showing the aforementioned results, the properties of the Bi2223 phase are not changed by the annealing in the oxygen atmosphere, while the Bi2212 phase contains oxygen to change the properties thereof and hence the critical current density J_c is improved at the low temperature of about 20 K in the overall wire.

[Table 1]

		Before Annealing	After Annealing
(1)	Performance of Bi2223 Phase (T_c and J_c under high and low temperatures)	→	unchanged
(2)	T_c of Bi2212 Phase	high	low
(3)	J_c of Bi2212 Phase under High Temperature (about 77 K)	high	low (for the above reason (2))
(4)	J_c of Bi 2212 Phase under Low Temperature (not more than 20 K)	low	high
(5)	J_c of Overall Wire under High Temperature (about 77 K)	high	low (for the above reasons (1) + (3))
(6)	J_c of Overall Wire under Low Temperature (not more than 20 K)	low	high (for the above reasons (1) + (4))

The annealing temperature is so set to at least 300°C and not more than 600°C that the Bi2212 phase can effectively contain oxygen and decomposition of the Bi2223 phase can be prevented. In other words, no oxygen is introduced into/discharged from the Bi2212 phase if the annealing temperature is less than 300°C, while the main Bi2223

phase is decomposed if the annealing temperature exceeds 700°C.

Preferably, the aforementioned manufacturing method further comprises a step of twisting the wire in advance of the heat treatment step. Thus, the twisted oxide superconducting wire can be inhibited from formation of blisters, and the critical current density can be improved.

Preferably in the aforementioned manufacturing method, the wire is not rolled. Thus, a round oxide superconducting wire can be inhibited from formation of blisters.

Preferably in the aforementioned manufacturing method, a wire formed by covering a ceramic-covered rod, obtained by covering the raw material powder with ceramic, with the metal is prepared in the step of preparing the wire formed by covering the raw material powder of the oxide superconductor with the metal. Thus, the oxide superconducting wire having a ceramic covering layer can be inhibited from formation of blisters.

Preferably, the aforementioned manufacturing method further comprises a step of molding the wire into a coil in advance of the heat treatment step. Thus, deterioration of the critical current value in the coil of the oxide superconducting wire can be effectively suppressed while inhibiting the wire from blistering.

Preferably in the aforementioned manufacturing method, the wire is held under a decompressed atmosphere before the pressurization in the heat treatment step is started.

Preferably in the aforementioned modifying method, the oxide superconducting wire is held under a decompressed atmosphere before the pressurization in the heat treatment step is started.

Thus, the pressure in the atmosphere does not exceed the pressure in the wire in the state before the pressurization in the heat treatment is started, whereby gas hardly penetrates into the wire, and formation of blisters on the wire can be further suppressed. In the oxide superconducting wire according to the present invention, the sintering density of an oxide superconductor is at least 95 %, preferably at least 99 %.

When employing the method of manufacturing an oxide superconducting wire or

the method of modifying an oxide superconducting wire according to the present invention, it is possible to obtain an oxide superconducting wire having an oxide superconductor exhibiting a high sintering density, which has been conventionally unmanufacturable. Further, the critical current density of the oxide superconducting wire can be improved by increasing the sintering density of the oxide superconductor in the oxide superconducting wire.

Throughout the specification, the term "Bi2223 phase" denotes a Bi-Pb-Sr-Ca-Cu-O oxide superconducting phase containing bismuth, lead, strontium, calcium and copper in atomic ratios of (bismuth and lead):strontium:calcium:copper approximately expressed as 2:2:2:3, more specifically a $(\text{BiPb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+z}$ superconducting phase.

Further, the term "Bi2212 phase" denotes a Bi-Pb-Sr-Ca-Cu-O oxide superconducting phase containing bismuth, lead, strontium, calcium and copper in atomic ratios of (bismuth and lead):strontium:calcium:copper approximately expressed as 2:2:1:2, more specifically a $(\text{BiPb})_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+z}$ superconducting phase.

Effects of the Invention

According to the inventive method of manufacturing an oxide superconducting wire, the pressure is applied to the wire while the 0.2 % yield strength of the metal is smaller than the total pressure of the pressurized atmosphere in the heat treatment. Thus, the portion of the metal is readily compressed through the compressive force resulting from the pressurization due to an effect similar to that of hot working. Therefore, the wire is compressed before the pressurizing gas penetrates into the wire through pinholes, whereby formation of voids and blisters can be sufficiently suppressed by the pressurization. Consequently, the sintering density of the oxide superconductor can be improved, and the critical current density of the oxide superconducting wire can be improved.

Brief Description of the Drawings

[Fig. 1] A diagram showing a partially fragmented perspective view conceptually illustrating the structure of an oxide superconducting wire.

[Fig. 2] A diagram showing manufacturing steps for an oxide superconducting wire according to a first embodiment of the present invention.

[Fig. 3] A schematic sectional view of a hot isostatic pressing (HIP) apparatus.

5 [Fig. 4] (a) to (d) are conceptual diagrams showing behavior of voids between oxide superconducting crystals stepwise.

[Fig. 5] A diagram showing the relation between total pressures P (MPa) of a pressurized atmosphere and numbers (/10 m) of blisters on a wire.

[Fig. 6] A diagram showing total pressures and partial oxygen pressures as to a gas mixture containing about 80 % of nitrogen and about 20 % of oxygen.

10 [Fig. 7] A diagram showing the relation between total pressures and oxygen concentration values in a case of setting the partial oxygen pressure constant.

[Fig. 8] A partially fragmented perspective view conceptually showing the structure of an oxide superconducting wire having pinholes.

15 [Fig. 9A] A graph showing thicknesses of an oxide superconducting wire having no pinholes before and after a heat treatment in a pressurized atmosphere.

[Fig. 9B] A graph showing thicknesses of an oxide superconducting wire having pinholes before and after a heat treatment in a pressurized atmosphere.

[Fig. 10] A diagram showing the relation between temperatures and pressures in a heat treatment step and time in a second embodiment of the present invention.

20 [Fig. 11] A diagram showing exemplary relation between temperatures, total pressures and partial oxygen pressures at a heat-up time before a heat treatment and in the heat treatment and time in a third embodiment of the present invention.

[Fig. 12] A diagram showing the relation between pressing speeds and sintering densities under various temperatures for starting pressurization.

25 [Fig. 13] A diagram showing temperature dependency of 0.2 % yield strength of silver.

[Fig. 14] A diagram showing the relation between sintering densities of oxide superconductors and critical current values of oxide superconducting wires.

[Fig. 15] A diagram showing exemplary relation between temperatures, total pressures and partial oxygen pressures in a case of performing annealing after a heat treatment in a fourth embodiment of the present invention and time.

5 [Fig. 16] A diagram showing critical current values of oxide superconducting wires before annealing and after annealing at a temperature of 500°C under respective temperatures.

[Fig. 17] A partially fragmented perspective view conceptually showing the structure of a twisted oxide superconducting wire.

10 [Fig. 18] A diagram showing manufacturing steps for the twisted oxide superconducting wire.

[Fig. 19] A partially fragmented perspective view schematically showing a state of twisting a multifilamentary wire.

[Fig. 20] A partially fragmented perspective view conceptually showing the structure of a round oxide superconducting wire.

15 [Fig. 21] A sectional view conceptually showing the structure of an oxide superconducting wire having a ceramic covering layer.

[Fig. 22] A diagram schematically showing a first step of a method of manufacturing an oxide superconducting wire according to a sixth embodiment of the present invention.

20 [Fig. 23] A diagram schematically showing a second step of the method of manufacturing an oxide superconducting wire according to the sixth embodiment of the present invention.

25 [Fig. 24] A diagram schematically showing a third step of the method of manufacturing an oxide superconducting wire according to the sixth embodiment of the present invention.

[Fig. 25] A perspective view showing the structure of a coiled oxide superconducting wire.

[Fig. 26] A diagram showing manufacturing steps for an oxide superconducting

wire according to a seventh embodiment of the present invention.

Description of the Reference Signs

1, 1a, 1b oxide superconducting wire, 2, 2a to 2c oxide superconductor filament, 3, 3a to 3c sheath part, 4 gas inlet, 5 top cover, 6 pressure vessel cylinder, 7 thermal barrier, 8 treated object, 9 heater, 10 bearer, 11 bottom cover, 12 superconducting crystal, 13 apparatus, 14 pinhole, 21 ceramic covering layer, 22 ceramic-covered rod, 25 rod.

Best Modes for Carrying Out the Invention

Embodiments of the present invention are now described with reference to the drawings.

(First Embodiment)

Fig. 1 is a partially fragmented perspective view conceptually showing the structure of an oxide superconducting wire.

A multifilamentary oxide superconducting wire, for example, is described with reference to Fig. 1. An oxide superconducting wire 1 has a plurality of oxide superconductor filaments 2 extending in the longitudinal direction and a sheath part 3 covering the same. The material for each of the plurality of oxide superconductor filaments 2 preferably has a Bi-Pb-Sr-Ca-Cu-O composition, for example, and a material including a Bi2223 phase having atomic ratios of (bismuth and lead):strontium:calcium:copper approximately expressed as 2:2:2:3 is optimum in particular. The material for the sheath part 3 consists of silver, for example.

While a multifilamentary wire has been described in the above, an oxide superconducting wire having a single-filamentary wire structure comprising a single oxide superconductor filament 2 covered with a sheath part 3 may alternatively be employed.

A method of manufacturing the aforementioned oxide superconducting wire is now described.

Fig. 2 is a diagram showing manufacturing steps for the oxide superconducting

wire according to the first embodiment of the present invention.

Referring to Fig. 2, raw material powder of an oxide superconductor is first filled into a metal tube (step S1). The raw material powder of the oxide superconductor consists of a material including a Bi2223 phase, for example.

5 Silver or a silver alloy having high heat conductivity is preferably employed for the metal tube. Thus, heat generated when the superconductor partially causes quenching can be quickly removed from the metal tube.

Then, the aforementioned wire is wiredrawn thereby forming a single-filamentary wire having a core material of a precursor covered with a metal such as silver (step S1a).
10 Then, a large number of such single-filamentary wires are bundled and fitted into a metal tube of a metal such as silver, for example (multifilamentary fitting: step S1b). Thus, a wire of a multifilamentary structure having a large number of core materials of the raw material powder is obtained. Then, the wire of the multifilamentary structure is wiredrawn thereby forming a multifilamentary wire of the raw material powder
15 embedded in a sheath part of silver or the like, for example (step S2). Thus, a multifilamentary wire formed by covering the raw material powder of the oxide superconductor with the metal is obtained.

Primary rolling is performed on this wire (step S3), followed by a first heat treatment (step S4). An oxide superconducting phase is generated from the raw material powder
20 due to these operations. Secondary rolling is performed on this heat-treated wire (step S5). Thus, voids resulting from the first heat treatment are removed. A second heat treatment is performed on the secondarily rolled wire (step S6). Sintering of the oxide superconducting phase progresses while the oxide superconducting phase is simultaneously converted to a single phase through the second heat treatment.

25 The oxide superconducting wire shown in Fig. 1, for example, can be manufactured according to the aforementioned manufacturing method.

In this embodiment, at least either the first heat treatment (step S4) or the second heat treatment (step S6) is performed in a pressurized atmosphere to which a pressure of

at least 1 MPa and less than 50 MPa is applied as the total pressure.

The heat treatment in this pressurized atmosphere is performed by hot isostatic pressing (HIP), for example. This hot isostatic pressing is now described.

Fig. 3 is a schematic sectional view of an apparatus for performing hot isostatic pressing (HIP).

Referring to Fig. 3, an apparatus 13 for performing hot isostatic pressing is constituted of a pressure vessel cylinder 6, a top cover 5 and a bottom cover 11 closing both ends of the pressure vessel cylinder 6, a gas inlet 4 provided on the top cover 5 for introducing gas into the pressure vessel cylinder 6, a heater 9 heating a treated object 8, a thermal barrier 7 and a bearer 10 supporting the treated object 8.

According to this embodiment, the bearer 10 supports the wire obtained by filling the raw material powder into the metal tube and thereafter wiredrawing/rolling the same as the treated object 8 in the pressure vessel cylinder 6. In this state, prescribed gas is introduced into the pressure vessel cylinder 6 through the gas inlet 4 thereby forming a pressurized atmosphere of at least 1 MPa and less than 50 MPa in the pressure vessel cylinder 6 and heating the wire 8 with the heater 9 to a prescribed temperature under this pressurized atmosphere. This heat treatment is preferably performed in an oxygen atmosphere, and the partial oxygen pressure is preferably at least 0.003 MPa and not more than 0.02 MPa. Thus, the wire 8 is subjected to the heat treatment by hot isostatic pressing.

According to this embodiment, the heat treatment is performed in the pressurized atmosphere of at least 1 MPa and less than 50 MPa as hereinabove described, to mainly attain the following three effects:

First, the number of voids formed between oxide superconducting crystals in the heat treatment can be reduced.

The inventors have found that the number of voids formed between oxide superconducting crystals mainly in a heat treatment can be remarkably reduced by performing the heat treatment in a pressurized atmosphere of at least 1 MPa as

compared with a case of less than 1 MPa.

Figs. 4(a) to (d) are conceptual diagrams showing behavior of voids between oxide superconducting crystals stepwise.

Referring to Figs. 4(a) to (d), the contact area between oxide superconducting crystals 12 formed in a heat treatment increases due to plastic flow when the heat treatment is performed in a pressurized atmosphere, to reduce the number of voids of several μm to several 10 μm present between the superconducting crystals 12 (Fig. 4(a) \rightarrow Fig. 4(b)). When held in this state, creep deformation is caused as shown in Fig. 4(c) so that voids present on the junction interface shrink while a contaminative portion such as an oxide film is partially broken/decomposed to cause diffusion of atoms and progress sintering. The voids between the superconducting crystals 12 finally substantially disappear as shown in Fig. 4(d), and a stable junction interface is formed.

To pass a current through a superconducting wire is to pass a current between superconducting crystals constituting the superconducting wire. What limits the quantity of a current passable while keeping a superconducting state (causing no electric resistance) in a refrigerant (e.g., liquid nitrogen or helium, or a refrigerator) for employing a superconducting wire is generally the junction between superconducting crystals having a weak superconducting state (the superconducting crystals have stronger superconductivity than the junction between the crystals). Voids inevitably remain in the junction between the superconducting crystals in normal atmospheric sintering. When the number of voids between the superconducting crystals is reduced, therefore, the performance of the superconducting wire is so improved that reduction of the critical current density can be prevented.

More specifically, the sintering density of an oxide superconductor heat-treated in the atmospheric pressure was 80 to 90% as to an oxide superconducting wire containing a Bi2223 phase, while the sintering density of an oxide superconductor prepared by setting the total pressure of a pressurized atmosphere to 10 MPa was 93 to 96 %, and reduction of the number of voids formed between oxide superconducting

crystals was observed.

Second, the oxide superconducting wire can be prevented from blisters formed in the heat treatment.

The inventors have investigated the number of blisters formed in a heat-treated wire when varying the total pressure for heat-treating an oxide superconducting wire in a pressurized atmosphere. Fig. 5 is a diagram showing the relation between total pressures P (MPa) of a pressurized atmosphere and numbers (/10 m) of blisters of a wire. Referring to Fig. 5, it is understood that the number of blisters in the oxide superconducting wire is remarkably reduced when the total pressure of the pressurized atmosphere exceeds 0.5 MPa and the blisters in the oxide superconducting wire substantially disappear when the total pressure is in excess of 1 MPa. Such results have been obtained conceivably for the following reason:

Powder of an oxide superconductor is generally filled into a metal tube at a filling factor of about 80 % of the theoretical density before sintering, and hence gas is present in voids of the powder. The gas in the voids of the powder causes cubic expansion when reaching a high temperature in a heat treatment, to blister the wire. According to this embodiment, however, the heat treatment is performed in the pressurized atmosphere of at least 1 MPa, and hence the pressure outside the metal tube can increase beyond that in the metal tube. Thus, the wire is conceivably prevented from blisters caused by the gas in the voids of the powder.

The inventors have further studied the cause for blisters of the wire, to also recognize that adsorbates such as carbon (C), water (H_2O) and oxygen (O_2) adhering to the raw material powder of the oxide superconductor are vaporized during sintering and the volume in the metal tube expands due to this gas to blister the wire. However, such blisters of the wire resulting from vaporization of the adsorbates to the powder can also conceivably be prevented since the external pressure can increase beyond the intermetallic internal pressure by performing the heat treatment in the pressurized atmosphere of at least 1 MPa.

Thus, it is conceivably possible to substantially remove not only blisters resulting from the gas present in the voids of the raw material powder of the oxide superconductor but also blisters resulting from vaporization of the adsorbates adhering to the surfaces of particles thereof. The blisters of the oxide superconducting wire cause reduction of the critical current density, and hence reduction of the critical current density can be prevented by preventing the wire from blisters.

Third, the partial oxygen pressure can be readily controlled in the heat treatment.

The inventors have found that a 2223 phase of a Bi-based oxide superconductor is stably formed when the partial oxygen pressure is controlled to at least 0.003 MPa and not more than 0.02 MPa regardless of the total pressure. A non-superconducting phase such as Ca_2PbO_4 is formed if the partial oxygen pressure exceeds 0.02 MPa, while the Bi2223 phase is hardly formed and the critical current density is reduced if the partial oxygen pressure is less than 0.003 MPa.

Fig. 6 is a diagram showing total pressures and partial oxygen pressures as to a gas mixture containing about 80 % of nitrogen and about 20 % of oxygen. Fig. 7 is a diagram showing the relation between total pressures and oxygen concentration values in a case of setting the partial oxygen pressure constant.

Referring to Fig. 6, a Bi2223 phase is stably formed without controlling the partial oxygen pressure when the total pressure of the pressurized atmosphere is the atmospheric pressure of 1 atm (0.1 MPa), for example, since the partial oxygen pressure is equivalent to the level of 0.2 atm (0.02 MPa) shown by a dotted line. As the total pressure of the pressurized atmosphere increases to 2 atm, 3 atm ..., however, the partial oxygen pressure also increases to exceed the level of 0.2 atm shown by the dotted line. Consequently, the Bi2223 phase is not stably formed. Therefore, the partial oxygen pressure must be controlled to at least 0.003 MPa and not more than 0.02 MPa by varying the mixing ratio of oxygen gas in a gas mixture, as shown in Fig. 7. A dotted line in Fig. 7 shows the level of 0.2 atm (0.02 MPa) similarly to the dotted line in Fig. 6.

In practice, the partial oxygen pressure is controlled by monitoring the total

pressure and the oxygen concentration. In other words, the partial oxygen pressure is calculated by multiplying the value of the total pressure by the oxygen concentration. Therefore, if the total pressure is 50 MPa, for example, the oxygen concentration is 0.01 % when the heat treatment is performed with a partial oxygen pressure of 0.005 MPa. Therefore, the injected gas mixture must be controlled by measuring the oxygen concentration of 0.01 %. However, the oxygen concentration of 0.01 % is substantially identical to a measurement error, and hence it is difficult to control the oxygen gas in the injected gas mixture by correctly measuring this oxygen concentration. According to this embodiment, the total pressure in the pressurized atmosphere is set to less than 50 MPa so that the concentration of the oxygen gas in the injected gas mixture can be kept high to some extent by reducing influence by a measurement error of the oxygen concentration, whereby the partial oxygen pressure can be readily controlled.

While this embodiment has been with reference to the case of constituting the pressurized atmosphere of nitrogen and oxygen, the pressurized atmosphere may be constituted of rare gas and oxygen. Therefore, the pressurized atmosphere may be constituted of argon and oxygen, for example.

(Second Embodiment)

It has been recognized that formation of voids and blisters can be effectively suppressed by performing a heat treatment in the aforementioned pressure range (at least 1 MPa and less than 50 MPa) when a wire formed by covering raw material powder of an oxide superconducting wire with a metal has no pinholes while formation of voids and blisters cannot be sufficiently suppressed by merely performing a heat treatment in the aforementioned pressure range when the wire has pinholes.

Fig. 8 is a partially fragmented perspective view conceptually showing the structure of an oxide superconducting wire having pinholes. Referring to Fig. 8, pinholes 14 are formed to pass from outside up to oxide superconductor filaments 2. The remaining structure shown in Fig. 8 is substantially identical to the structure shown in Fig. 1, and hence identical members are denoted by identical reference numerals and

redundant description is not repeated.

Fig. 9A is a graph showing thicknesses of an oxide superconducting wire having no pinholes before and after a heat treatment step in a pressurized atmosphere, and Fig. 9B is a graph showing thicknesses of an oxide superconducting wire having pinholes before and after a heat treatment step. Heat treatment conditions in Figs. 9A and 9B are a total pressure of 20 MPa, a partial oxygen pressure of 0.008 MPa, a temperature of 825°C in an atmosphere, and a heat treatment time of 50 hours.

Referring to Fig. 9A, the thickness of the oxide superconducting wire having no pinholes is reduced by about 0.006 mm to 0.01 mm after the heat treatment. This is because formation of voids between oxide superconducting crystals and blisters of the oxide superconducting wire is suppressed due to the heat treatment in a pressurized atmosphere having the total pressure of 20 MPa.

Referring to Fig. 9B, on the other hand, the thickness of the oxide superconducting wire having pinholes is reduced only by about 0.002 mm to 0.005 mm after the heat treatment, and formation of voids between oxide superconducting crystals and blisters of the oxide superconducting wire is not sufficiently suppressed. The thickness of a portion (portion A) having pinholes in the wire increases after the heat treatment as compared with that before the heat treatment.

Thus, it has been recognized that formation of voids and blisters can be effectively suppressed by performing the heat treatment in the aforementioned pressure range (at least 1 MPa and less than 50 MPa) when there are no pinholes while formation of voids and blisters cannot be sufficiently suppressed by merely performing the heat treatment in the aforementioned pressure range when there are pinholes.

In the heat treatment in the pressurized atmosphere according to the present invention, plastic flow and creep deformation take place in the superconducting crystals formed in the heat treatment due to the high pressure of at least 1 MPa outside the wire, whereby voids between the oxide superconducting crystals formed in the heat treatment are suppressed. Further, the gas in the voids of the oxide superconducting crystal

powder formed in the heat treatment or the gas adhering to the oxide superconducting crystal powder formed in the heat treatment can be inhibited from expansion in the heat treatment due to the pressure from outside the metal tube, whereby the oxide superconducting wire is inhibited from formation of blisters. Consequently, reduction of the critical current density resulting from voids and blisters is prevented.

In a wire having pinholes, however, pressurizing gas penetrates into the wire through the pinholes also when the aforementioned heat treatment in the pressurized atmosphere is performed. Therefore, no difference is caused between the internal and external pressures of the wire and formation of voids and blisters is not sufficiently suppressed by the heat treatment in the pressurized atmosphere. Consequently, the effect of preventing reduction of the critical current density is reduced.

Referring to Fig. 8, the thickness W of a sheath part 3 may be increased, in order not to form the pinholes 14 passing from outside up to oxide superconductor filaments 2. If the thickness W of the sheath part 3 is increased, however, the ratio of the oxide superconductor filaments 2 in an oxide superconducting wire 1 is reduced to reduce the quantity of current passable per unit area. Therefore, the inventors have made deep studies, to find that formation of voids and blisters can be suppressed for improving the critical current density without increasing the thickness W of the sheath part 3 also in a wire having pinholes by employing a technique described below.

According to this technique, pressurization is performed at a speed of at least 0.05 MPa/min. at a heat-up time before a heat treatment in at least either a first heat treatment (step S4) or a second heat treatment (step S6). In the heat treatment, the total pressure in the atmosphere is controlled to continuously increase. In cool-down time immediately after the heat treatment, further, control is made to compensate for reduction of the pressure resulting from temperature reduction (to add a pressure).

Fig. 10 is a diagram showing the relation between temperatures and pressures in a heat treatment step and time in a second embodiment of the present invention.

Referring to Fig. 10, the pressure is gently increased according to the state

equation of gas at a heat-up time before the heat treatment if the temperature of the atmosphere is not more than 700°C, for example. When the temperature of the atmosphere substantially exceeds 700°C, the pressure in the atmosphere is increased to about 10 MPa. At this time, the pressure in the atmosphere is increased at a blast with a pressing speed of at least 0.05 MPa/min.

The inventors have found that the speed of pressurizing gas penetrating into a wire through pinholes is less than about 0.05 MPa/min. when an oxide superconducting wire having the pinholes is heat-treated in a pressurized atmosphere. Therefore, the pressure in the atmosphere can be kept higher than that in the wire at the heat-up time before the heat treatment by controlling the total pressure of the atmosphere to continuously increase at a speed of at least 0.05 MPa/min. at the heat-up time before the heat treatment.

Thereafter the temperature is kept at 830°C, for example, in the heat treatment. On the other hand, the pressure in the atmosphere is continuously increased. While the pressing speed in the heat treatment is preferably as high as possible, the total pressure exceeds 50 MPa if the pressing speed is excessively high and hence the pressure must be continuously increased at such a proper pressing speed that the total pressure in the heat treatment does not exceed 50 MPa. Referring to Fig. 16, the pressure is increased to about 30 MPa. Therefore, the time when the pressure in the wire and that in the atmosphere are equalized with each other can be retarded from a time t_1 to a time t_2 as compared with a case where the pressure is kept constant in the heat treatment. Thus, the state where the pressure in the atmosphere is higher than that in the wire can be continuously kept longer in the heat treatment.

Thereafter in cool-down time immediately after the heat treatment, the pressure starts to lower according to the state equation of gas following reduction of the temperature in the atmosphere. At this time, the pressure is controlled to compensate for reduction of the pressure resulting from temperature reduction (to add a pressure). In order to form a stable oxide superconducting phase, the partial oxygen pressure is

controlled to be regularly in the range of 0.003 to 0.02 MPa.

According to this technique, the pressure in the atmosphere increases beyond that in the wire at the heat-up time before the heat treatment, whereby compressive force can be applied to the wire. Further, the state where the pressure in the atmosphere is higher than that in the wire can be continuously kept longer in the heat treatment. Consequently, formation of voids and blisters is suppressed at the heat-up time before the heat treatment and at the heat-up time, whereby reduction of the critical current density can be effectively suppressed due to the heat treatment in the pressurized atmosphere of at least 1 MPa and less than 50 MPa.

(Third Embodiment)

The inventors have further made deep studies, to find that the critical current density of an oxide superconducting wire can be further improved by employing a technique described below.

According to this technique, pressurization is started when the temperature of the atmosphere exceeds 400°C, preferably 600°C at the heat-up time before the heat treatment in at least either the first heat treatment step (step S4) or the second heat treatment step (step S6) shown in Fig. 2. The pressurization is preferably performed at a pressing speed of at least 0.05 MPa/min. more preferably at least 0.1 MPa/min.

Fig. 11 is a diagram showing exemplary relation between temperatures, total pressures and partial oxygen pressures at a heat-up time before a heat treatment and in the heat treatment and time in a third embodiment of the present invention.

Referring to Fig. 11, the temperature of the atmosphere is gently increased up to 820°C. The pressure of the atmosphere is gently increased according to a state equation of gas when the temperature is less than 600°C. Pressurization is started after the temperature of the atmosphere reaches 600°C, and performed up to about 25 MPa at a pressing speed of about 0.1 MPa/min. The partial oxygen pressure is held in the range of at least 0.003 MPa and less than 0.02 MPa. The critical current density of an oxide superconducting wire can be further improved by performing a heat treatment under

these conditions. In order to confirm the effect of the aforementioned heat treatment method, the inventors have made the following experiment:

Fig. 12 is a diagram showing the relation between pressing speeds and sintering densities under various temperatures for starting pressurization.

5 Referring to Fig. 12, the sintering densities of oxide superconductor filaments (oxide superconductors) are about 93 % to 96 % at pressing speeds of at least 0.05 MPa/min. in a case of starting pressurization when the temperature of an atmosphere is 30°C. In a case of starting pressurization after the temperature of the atmosphere reaches 400°C, on the other hand, the sintering densities of the oxide superconductor
10 filaments are at least about 95 % at the pressing speeds of at least 0.05 MPa/min. In a case of starting pressurization after the temperature of the atmosphere reaches 600°C, further, the sintering densities of the oxide superconductor filaments are at least about 97 % at the pressing speeds of at least 0.05 MPa/min., and the sintering densities of the oxide superconductor filaments are at least about 98 % at pressing speeds of at least 0.1
15 Pa/min. In both cases of starting pressurization after the temperature of the atmosphere reaches 400°C and 600°C respectively, in addition, the sintering densities of the oxide superconductor filaments are at least about 99 % at pressing speeds of at least 0.15 MPa/min. The sintering density is improved at a pressing speed of at least 0.05 MPa/min. conceivably because the speed of pressurizing gas penetrating into the wire
20 through pinholes is less than about 0.05 MPa/min. and the pressure in the atmosphere can be regularly kept higher than that in the wire since the wire is pressurized at a speed faster than this penetration speed. It is understood from the results shown in Fig. 12 that the sintering density of the oxide superconductor filaments is improved when the pressurization is started after the temperature of the atmosphere exceeds 400°C,
25 preferably 600°C. It is also understood that the sintering density of the oxide superconductor filaments is further improved when the speed of pressurization is set to preferably at least 0.05 MPa/min. more preferably at least 0.1 MPa/min. This is conceivably for the following reason:

Fig. 13 is a diagram showing temperature dependency of 0.2 % yield strength of silver.

Referring to Fig. 13, the 0.2 % yield strength of silver is about 370 MPa when an atmosphere is at the room temperature, and reduced as the temperature of the atmosphere is increased. In other words, the 0.2 % yield strength is reduced to about 50 MPa when the temperature of the atmosphere reaches 400°C, and the 0.2 % yield strength is reduced to about 25 MPa when the temperature of the atmosphere reaches 600°C. Thus, the 0.2 % yield strength of silver is reduced to a level substantially identical to the total pressure (at least 1 MPa and less than 50 MPa) of the aforementioned pressurized atmosphere when the temperature of the atmosphere is 400°C. Further, the 0.2 % yield strength of silver is reduced to about half the total pressure (at least 1 MPa and less than 50 MPa) of the aforementioned pressurized atmosphere when the temperature of the atmosphere is 600°C. According to the aforementioned technique, it follows that a pressure is applied to the wire when the strength of the sheath part is reduced to a level substantially identical to the total pressure of the pressurized atmosphere. Therefore, the sheath part is readily compressed through compressive force resulting from pressurization due to an effect similar to that of hot working. Consequently, the wire is compressed before the pressurizing gas penetrates into the wire through pinholes, whereby formation of voids and blisters can be sufficiently suppressed by the pressurization, and the sintering density of the oxide superconducting filaments can be improved. The 0.2 % yield strength values shown in Fig. 13 are values obtained by performing a tensile test defined in JIS (Japanese Industrial Standards) on pure silver wires of 1.5 mm in diameter.

The sintering densities of the oxide superconductor filaments shown in Fig. 12 are calculated by the following method: First, each oxide superconducting wire of 5 g ($= M_t$ (g)) is cut out. Then, the cut oxide superconducting wire is dipped in alcohol, for measuring the weight (W (g)) of the wire in alcohol and calculating floatage acting on the oxide superconducting wire. The volume (V_t (cm³)) of the oxide superconducting

wire is calculated through the known alcohol density ($\rho = 0.789 \text{ (g/ cm}^3\text{)}$). More specifically, the volume V_t is calculated according to the following equations (1) and (2), assuming that F_t represents the flotage:

$$F_t = M_t - W \dots (1)$$

$$5 \quad V_t = F_t / \rho \dots (2)$$

Then, the oxide superconducting wire is dissolved in nitric acid and silver is determined by performing ICP (inductive coupled plasma) emission spectroscopy on the solution, for calculating the ratio (Y) of silver occupying the weight of the oxide superconducting wire. The weight ($M_f \text{ (g)}$) of an oxide superconductor filament part and the weight ($M_s \text{ (g)}$) of a sheath part are calculated from the weight of the oxide superconducting wire according to the following equations (3) and (4):

$$M_s = M_t \times Y \dots (3)$$

$$M_f = M_t - M_s \dots (4)$$

Then, the volume ($(V_s \text{ (cm}^3\text{)})$) of the sheath part is calculated from the known silver gravity ($10.5 \text{ (g/cm}^3\text{)}$), and the volume ($(V_f \text{ (cm}^3\text{)})$) of oxide superconductor filaments is calculated from the volume of the sheath part. The density ρ_f of the oxide superconductor filaments is calculated from the volume of the oxide superconductor filaments. More specifically, the density ρ_f is calculated according to the following equations (5) to (7):

$$20 \quad V_s = M_s / 10.5 \dots (5)$$

$$V_f = V_t - V_s \dots (6)$$

$$\rho_f = M_f / V_f \dots (7)$$

On the other hand, a value 6.35 g/cm^3 is employed as the theoretical density of the oxide superconductor filaments. This value is calculated by the following method:

25 The atomic ratio of a Bi2223 phase in the oxide superconductor filaments is calculated by ICP emission spectroscopy and EDP (energy dispersive X-ray spectroscopy) analysis. The lattice constant of the Bi2223 phase is obtained by X-ray analysis, for calculating the values of a- and c-axes. The theoretical density is calculated from these values.

The sintering density of the oxide superconductor filaments is calculated from the ratio between the density of the oxide superconductor filaments obtained by the aforementioned method and the theoretical density of the oxide superconductor filaments. More specifically, the sintering density is calculated according to the following equation (8):

$$\text{Sintering Density (\%)} = (\rho / \rho_0) \times 100 \dots (8)$$

Fig. 14 is a diagram showing the relation between sintering densities of oxide superconductors and critical current values of oxide superconducting wires.

Referring to Fig. 14, the critical current values of oxide superconducting wires having sintering densities of not more than about 95 % are less than 80 A, while the critical current values of oxide superconducting wires having sintering densities of at least about 95 % are mainly in the range exceeding 80 A. The critical current value is obtained by multiplying the critical current density by the sectional area of oxide superconductor filaments, and hence the critical current density is proportionate to the critical current value. Therefore, the critical current density is improved in an oxide superconducting wire having a high sintering density. This is conceivably because a large quantity of current flows to superconducting filaments in the oxide superconducting wire having a high sintering density due to a small number of voids between crystals of the superconducting filaments.

It is understood from the aforementioned results shown in Figs. 12 and 14 that the sintering density of the oxide superconductor filaments is improved and the critical current density of the oxide superconducting wire is improved when pressurization is started after the temperature of the atmosphere exceeds 400°C, preferably 600°C, at a speed of preferably at least 0.05 MPa/min., more preferably at least 0.1 MPa/min.

According to the method of manufacturing the oxide superconducting wire of this embodiment, a pressure is applied to the wire when the 0.2 % yield strength of the sheath part is reduced to a level substantially identical to the total pressure of the pressurized atmosphere in the heat treatment. Thus, the sheath part is readily

compressed through compressive force resulting from the pressurization due to an effect similar to that of hot working. Therefore, the wire is compressed before the pressurizing gas penetrates into the wire through pinholes, whereby formation of voids and blisters can be sufficiently suppressed due to the pressurization. Consequently, the sintering density of the oxide superconductor filaments can be improved, and the critical current density of the oxide superconducting wire can be improved.

Preferably in the aforementioned manufacturing method, the pressurization is started after the temperature of the atmosphere exceeds 600°C at the heat-up time before the heat treatment in the heat treatment step.

Thus, a pressure is applied to the wire while the 0.2 % yield strength of the sheath part is reduced to about half the total pressure of the pressurized atmosphere in the heat treatment. Therefore, the sheath part is further readily compressed through the compressive force resulting from the pressurization. Consequently, the sintering density of the filaments of the oxide superconducting wire can be further improved, and the critical current density of the oxide superconducting wire can be further improved.

Preferably in the aforementioned manufacturing method, the speed of the pressurization is at least 0.05 MPa/min. more preferably at least 0.1 MPa/min.

Thus, the sintering density of the oxide superconductor filaments can be further improved, and the critical current density of the oxide superconducting wire can be further improved.

Preferably in the aforementioned manufacturing method, the heat treatment step is carried out in an oxygen atmosphere, and the partial oxygen pressure is at least 0.003 MPa and not more than 0.02 MPa.

Thus, a stable oxide superconducting wire is formed, and the critical current density can be improved. A hetero phase is formed if the partial oxygen pressure exceeds 0.02 MPa, while the oxide superconducting phase is hardly formed and the critical current density is reduced if the partial oxygen pressure is less than 0.003 MPa.

Each of the first to third embodiments has been described with reference to the

method of improving the critical current density (method of manufacturing an oxide superconducting wire) by performing a prescribed heat treatment method in at least either the first heat treatment step (step S4) or the second heat treatment step (step S6) shown in Fig. 2. Alternatively, the present invention is also applicable as a heat
5 treatment step carried out on the manufactured oxide superconducting wire (i.e., the oxide superconducting wire after completion of the steps S1 to S6 in Fig. 2), i.e., a method of modifying an oxide superconducting wire, in place of the aforementioned case. In other words, an oxide superconducting wire having a sintering density of less than 95 % can be modified by applying the heat treatment according to the present
10 invention, for example, and an effect of modification is attained also in a case of applying the heat treatment according to the present invention to an oxide superconducting wire having a sintering density of at least 95 % and less than 99 %. Thus, the critical current density of an oxide superconducting wire can be improved also when the heat treatment according to the present invention is applied as a method of
15 modifying an oxide superconducting wire.

Further, each of the first to third embodiments has been described with reference to the case of heat-treating the oxide superconducting wire having the sheath part of silver in the pressurized atmosphere having the total pressure of at least 1 MPa and less than 50 MPa in the heat treatment and starting pressurization after the temperature of
20 the atmosphere exceeds 400°C at the heat-up time before the heat treatment in the heat treatment step. However, the present invention is not restricted to this case but is applicable to all oxide superconducting wires formed by covering oxide superconductors with metals. In this case, the heat treatment is performed in a pressurized atmosphere having a total pressure of at least 1 MPa and less than 50 MPa in the heat treatment, and
25 pressurization is started from a temperature reducing at least 0.2 % yield strength of the metal below the total pressure (at least 1 MPa and less than 50 MPa) in the heat treatment at a heat-up time before the heat treatment in the heat treatment step. Thus, a pressure is applied to the wire in a state where the 0.2 % yield strength of the metal is

smaller than the total pressure of the pressurized atmosphere in the heat treatment, whereby the portion of the metal is readily compressed through compressive force resulting from the pressurization. Thus, the sintering density of the oxide superconductor can be improved and the critical current density of the oxide superconducting wire can be improved due to reasons similar to those in the
5 aforementioned oxide superconducting wire having the sheath part of silver.

(Fourth Embodiment)

In general, a bismuth (Bi)-based oxide superconducting wire is known as one of oxide superconducting wires. This Bi-based oxide superconducting wire is usable at
10 the liquid nitrogen temperature, and can obtain a relatively high critical current density. Further, this Bi-based oxide superconducting wire, which is relatively easy to elongate, is expected for application to a superconducting cable or magnet. However, a conventional Bi-based oxide superconducting wire has been disadvantageously unsuitable to application requiring high performance under a low temperature, due to a
15 low critical current density (J_c) at a low temperature of about 20 K.

In relation to this, the inventors have found that the critical current density of a Bi-based oxide superconducting wire under a low temperature of about 20 K can be improved by combining the following technique with the technique according to each of the first to third embodiments. This technique is now described.

20 According to this technique, the wire is annealed in an atmosphere containing oxygen at a temperature of at least 300°C and not more than 600°C in at least either the first heat treatment step (step S4) or the second heat treatment step (step S6) shown in Fig. 2.

Fig. 15 is a diagram showing exemplary relation between temperatures, total pressures and partial oxygen pressures in a case of performing annealing after a heat
25 treatment in a fourth embodiment of the present invention and time.

Referring to Fig. 15, an oxide superconducting wire is held in an atmosphere having a temperature of 820°C and a total pressure of 25 MPa for a constant time, and

thereafter the temperature of the atmosphere is reduced. At this time, the total pressure of the atmosphere is also gently reduced. When the temperature and the pressure of the atmosphere reach about 300°C and about 16 MPa respectively, the oxide superconducting wire is held at a constant temperature and annealed for about 30 hours. While the wire is held at the constant temperature, the total pressure is further continuously gently reduced. The temperature of the atmosphere is reduced again after completion of the annealing. The partial oxygen pressure is about 0.008 MPa during the heat treatment, and increased to about 0.024 MPa during the annealing. The partial oxygen pressure is reduced along with the total pressure after the annealing.

In order to confirm the effect of the aforementioned annealing, the inventors have made the following experiment:

The inventors have investigated the degrees of improvement of critical current values I_c at 20 K as to a case of performing annealing and a case of performing no annealing in heat treatment steps. The annealing was performed for various annealing times under various partial oxygen pressures. Table 2 shows the averages of ratios of increase of critical current values $I_c(22\text{ K})$ at 22 K to critical current values $I_c(77\text{ K})$ at 77 K after the heat treatment steps as to respective samples. The critical current values were measured in a magnetic field of 3 T.

[Table 2]

Sample No.		Temperature	Time	Partial Oxygen Pressure	Average Value: $I_c(20\text{K})/I_c(77\text{K})$
1	unannealed				1.6
2	unannealed				1.7
3	unannealed				1.5
4	annealed	300°C	30 h.	24kPa	2.1
5	annealed	300°C	30 h.	12kPa	1.9
6	annealed	300°C	40 h.	20kPa	2

Referring to Table 2, the averages of the ratios of increase of the critical current values at 22 K in the case of performing no annealing are 1.6, 1.7 and 1.5 respectively. On the other hand, the averages of the ratios of increase of the critical current values at

22 K in the case of performing annealing are 2.1, 1.9 and 2 respectively. Thus, it is understood that the critical current value at 20 K can be improved in the case of performing annealing as compared with the case of performing no annealing.

In order to confirm the effect of annealing the wire in the atmosphere containing oxygen at the temperature of at least 300°C and not more than 600°C, the inventors have made the following experiment:

First, a tape-like Bi-based oxide superconducting wire of a multifilamentary structure having 61 filaments with external sizes of 4.2 mm in width and 0.24 mm in thickness and a silver ratio of 1.5 was prepared. Further, this oxide superconducting wire was heat-treated and annealed in this heat treatment. The annealing was performed in an oxygen jet for an annealing time of 20 hours under various annealing temperatures shown in Table 3. The quantity of a Bi2212 phase in the oxide superconductor was also varied. Table 3 also shows respective critical current values I_c at 77 K and 20 K before the annealing and respective critical current values I_c at 77 K and 20 K after the annealing as to respective samples.

Used wires were selected from the same lot, and it is assumed that the sectional areas of superconducting portions of respective wires are identical to each other. Therefore, the magnitude of the critical current value I_c in the following Table 3 is proportionate to the critical current density J_c ($J_c = I_c$ /sectional area of superconducting portion).

[Table 3]

Sample No.	Quantity of Bi2212 Phase (%)	Before Annealing 77K Ic(A)	Before Annealing 20K Ic(A)(1)	Annealing Temperature (°C)	After Annealing 77K Ic(A)	After Annealing 20K Ic(A)(2)	(2)/(1)
7	9	95	500	no	-	-	-
8	9	95	500	100	95	500	1.0
9	9	95	500	200	95	500	1.0
10	9	95	500	300	94	512	1.02
11	9	95	500	400	92	530	1.06
12	9	95	500	500	90	555	1.11
13	9	95	500	600	89	550	1.1
14	9	95	500	700	70	480	0.96
15	9	95	500	800	60	345	0.69
16	2	100	527	500	99	528	1.0
17	5	97	511	500	96	543	1.06
18	9	95	500	500	90	555	1.11
19	13	92	485	500	88	540	1.11
20	19	90	474	500	82	530	1.12
21	25	83	437	500	75	500	1.14
22	50	60	316	500	50	410	1.3

It is understood from the results shown in Table 3 that the critical current value I_c (critical current density J_c) at the low temperature (20 K) is improved as compared with that before the annealing due to the annealing performed in the oxygen atmosphere at the temperature of at least 300°C and not more than 600°C. It is also understood that the critical current value I_c after the annealing exceeds 530 A and the absolute value of the critical current value I_c (critical current density J_c) is increased due to the quantity of the Bi2212 phase in the oxide superconductor set to at least 5 mol % and not more than 20 mol %.

The inventors have also investigated the critical current values I_c of oxide superconducting wires at respective temperatures (K) before performing annealing and after performing the annealing at a temperature of 500°C. Fig. 16 shows the results.

It is understood from the results shown in Fig. 16 that the critical current value I_c of an annealed sample is higher than that of an unannealed sample from a temperature of not more than about 20 K.

In a method of manufacturing an oxide superconducting wire according to this embodiment, the oxide superconducting wire includes a Bi2223 phase, and is annealed in an oxygen-containing atmosphere at a temperature of at least 300°C and not more than 600°C. Thus, the critical current density of the oxide superconducting wire at a low temperature of about 20 K is improved.

This embodiment has been described with reference to a method of improving the critical current density by performing a prescribed heat treatment method in at least either the first heat treatment step (step S4) or the second heat treatment step (step S6) shown in Fig. 2. In place of this case, however, the present invention is also applicable to a heat treatment step carried out on the manufactured oxide superconducting wire (i.e., the oxide superconducting wire after completion of the steps S1 to S6 in Fig. 2), i.e., a method of modifying an oxide superconducting wire. The critical current density of an oxide superconducting wire can be improved also when the heat treatment according to the present invention is applied as a method of modifying an oxide

superconducting wire.

(Fifth Embodiment)

Each of the first to fourth embodiments has been described with reference to the manufacturing method in the case where the superconductor filaments 2 extend in the longitudinal direction of the oxide superconducting wire 1 and the oxide
5 superconducting wire 1 is in the form of a tape, as shown in Fig. 1. The oxide superconducting wire shown in Fig. 1 has a high critical current density. However, the manufacturing method according to the present invention is applicable to a method of manufacturing a twisted oxide superconducting wire, for example, in place of the
10 method of manufacturing the oxide superconducting wire shown in Fig. 1.

Fig. 17 is a partially fragmented perspective view conceptually showing the structure of a twisted oxide superconducting wire. As shown in Fig. 17, a twisted oxide superconducting wire 1a has a plurality of oxide superconductor filaments 2a extending in the longitudinal direction and a sheath part 3a covering the same. The oxide
15 superconductor filaments 2a are spirally twisted along the longitudinal direction of the oxide superconducting wire 1a. A method of manufacturing this twisted oxide superconducting wire 1a is now described.

Fig. 18 is a diagram showing manufacturing steps for the twisted oxide superconducting wire. Referring to Fig. 18, a wire is twisted so that twisting pitches are 500 mm, 100 mm, 50 mm and 10 mm respectively, for example, in a state of a round wire (step S2a)
20 after a multifilamentary wire is formed by wiredrawing (step S2) and before primary rolling (step S3) in the method of manufacturing the twisted oxide superconducting wire 1a. Fig. 19 shows the state of this twisting. The remaining manufacturing method is substantially similar to the manufacturing method according to the first embodiment, and
25 hence redundant description is not repeated.

The twisted oxide superconducting wire can effectively reduce AC loss. When the present invention is applied to a method of manufacturing a twisted oxide superconducting wire, the twisted oxide superconducting wire can be inhibited from

formation of blisters, and the critical current density can be improved.

The inventors have made a test in order to confirm the aforementioned effect. This test is now described.

Powder having composition ratios of Bi:Pb:Sr:Ca:Cu = 1.82:0.33:1.92:2.01:3.02 was prepared from Bi₂O₃, PbO, SrCO₃, CaCO₃ and CuO. This powder was heat-treated at a temperature of 750°C for 10 hours, and thereafter heat-treated at a temperature of 800°C for 8 hours. Thereafter a sintered body obtained through the heat treatments was pulverized in an automatic mortar. Powder obtained through the pulverization was heat-treated at a temperature of 850°C for 4 hours, and a sintered body obtained through the heat treatment was pulverized in an automatic mortar. The powder obtained through the pulverization was heat-treated, and thereafter filled into a silver pipe of 36 mm in outer diameter and 30 mm in inner diameter (step S1). Then, the silver pipe filled with the powder was wiredrawn for obtaining a single-filamentary wire (step S1a). Further, 61 such single-filamentary wires were bundled and fitted into a silver pipe of 36 mm in outer diameter and 31 mm in inner diameter (step S1b). Then, the silver pipe fitted with the plurality of single-filamentary wires was wiredrawn for obtaining a multifilamentary wire of 1.5 mm in diameter (step S2). Then, this multifilamentary wire was twisted at twisting pitches of 20 mm, 15 mm, 10 mm and 5 mm (step S2a). Thereafter primary rolling (step S3) was performed for obtaining a tape-shaped wire having a thickness of 0.26 mm, a width of 3.7 mm and a length of 100 m. Then, this wire was heat-treated at a temperature of 840°C in an atmosphere having an oxygen concentration of 8 % for 30 hours as a first heat treatment (step S4). Then, secondary rolling (step S5) was performed for drafting the wire by 8 %. Then, this wire was heat-treated at a temperature of 820°C in an atmosphere having a total pressure of 25 Pa and a partial oxygen pressure of 8 kPa for 50 hours as a second heat treatment (step S6). At a heat-up time before the second heat treatment (step S6), pressurization was started from a temperature reducing the 0.2 % yield strength of the silver pipe below 25 MPa. A sample 1 was prepared from the twisted oxide

superconducting wire 1a obtained through the aforementioned steps.

On the other hand, the steps S1 to S5 shown in Fig. 18 were carried out under conditions identical to the above and a wire was heat-treated at a temperature of 820°C in an atmosphere having the atmospheric pressure and a partial oxygen pressure of 8 kPa for 50 hours as a second heat treatment (step S6), for obtaining a twisted oxide superconducting wire of comparative example 1. The critical current densities were measured and the numbers of formed blisters were investigated as to the sample 1 and comparative example 1. Consequently, the critical current density of comparative example 1 was 2.0 kA/cm², while the critical current density of the sample 1 was 2.6 kA/cm², which was improved by about 1.3 times. While comparative example 1 caused 30 blisters per 100 m, the sample 1 caused absolutely no blisters. Thus, it is understood that formation of blisters on the twisted oxide superconducting wire can be suppressed and the critical current density can be improved according to the inventive manufacturing method.

The inventive manufacturing method is also applicable to a method of manufacturing a round oxide superconducting wire, for example.

Fig. 20 is a partially fragmented perspective view conceptually showing the structure of a round oxide superconducting wire. As shown in Fig. 20, a round oxide superconducting wire 1b has a plurality of oxide superconductor filaments 2b extending in the longitudinal direction and a sheath part 3b covering the same. The oxide superconducting wire 1b has a sectional shape close to a true circle.

The round oxide superconducting wire 1b is manufactured by not carrying out the primary rolling (step S3) and the secondary rolling (step S5) in the method of manufacturing an oxide superconducting wire shown in Fig. 2. The remaining manufacturing method is substantially similar to the manufacturing method according to the first embodiment, and hence redundant description is not repeated.

The round oxide superconducting wire can effectively reduce AC loss. When the present invention is applied to a method of manufacturing a round oxide

superconducting wire, the round oxide superconducting wire can be inhibited from formation of blisters, and the critical current density can be improved.

(Sixth Embodiment)

Each of the first to fourth embodiments has been described with reference to the manufacturing method in the case where the superconductor filaments extend along the longitudinal direction of the oxide superconducting wire and the oxide superconducting wire 1 has a tape-like shape. The fifth embodiment has been described with reference to the manufacturing method in the case where the oxide superconducting wire is a twisted wire or a round wire. In place of these methods of manufacturing oxide superconducting wires, the inventive manufacturing method is also applicable to a method of manufacturing an oxide superconducting wire having a ceramic covering layer, for example.

Fig. 21 is a sectional view conceptually showing the structure of an oxide superconducting wire having a ceramic covering layer. As shown in Fig. 21, an oxide superconducting wire 1c having a ceramic covering layer has a plurality of oxide superconductor filaments 2a extending in the longitudinal direction (direction of the plane of the figure), a ceramic covering layer 21 covering the plurality of oxide superconductor filaments 2c and a sheath part 3c covering the ceramic covering layer 21. The ceramic covering layer 21 is composed of a metallic oxide, for example, and converted to a non-superconductor at an operation temperature of the oxide superconducting wire 1c. A method of manufacturing the oxide superconducting wire 1c having this ceramic covering layer 21 is now described.

First, raw material powder is molded for forming a rod 25 of the raw material powder, as shown in Fig. 22. Then, the periphery of the rod 25 is covered with compressed ceramic powder through an extruder or the like, for forming a ceramic-covered rod 22 having the ceramic covering layer 22 covering the rod 25 as shown in Fig. 23. Then, a plurality of ceramic-covered rods 22 are fitted in the sheath part 3c, as shown Fig. 24. Thus, a wire of a multifilamentary structure having a large number of

filaments of the raw material powder is obtained. Then, the wire of the multifilamentary structure is wiredrawn for forming a multifilamentary wire embedded in the raw material silver sheath part 3c. Thus, a wire formed by covering the ceramic-covered rods, prepared by covering the raw material powder with ceramic, with the metal is obtained. Thereafter the steps S3 to S6 shown in Fig. 2 are carried out for completing the oxide superconducting wire 1c according to this embodiment shown in Fig. 21.

The oxide superconducting wire having a ceramic covering layer can effectively reduce AC loss. When the present invention is applied to a method of manufacturing an oxide superconducting wire having a ceramic covering layer, the oxide superconducting wire having a ceramic covering layer can be inhibited from formation of blisters, and the critical current density can be improved.

In order to confirm the aforementioned effect, the inventors have prepared an oxide superconducting wire having a ceramic covering layer through the manufacturing method according to this embodiment, and measured the critical current density. Consequently, the critical current density was improved to 1.4 times as compared with a case of performing both of two heat treatments in the atmosphere.

(Seventh Embodiment)

When an oxide superconducting wire is applied to a magnet or the like, employed is a substance prepared by winding the oxide superconducting wire in the form of a track reel-shaped coil as shown in Fig. 25. The oxide superconducting wire can be molded into a coil by a wind and react technique.

Fig. 26 is a diagram showing manufacturing steps for an oxide superconducting wire according to a seventh embodiment of the present invention. As shown in Fig. 26, the wind and react technique is a method of molding a wire into a coil (step S5a) immediately after secondary rolling (step S5) and thereafter performing a second heat treatment (step S6).

The wire not yet subjected to the second heat treatment (step S6) has stronger

flexural strength than the oxide superconducting wire completed through the second heat treatment (step S6). A flexural load is applied to the wire in the step of molding the same into a coil, and hence the coil of the oxide superconducting wire prepared through the wind and react technique is advantageously smaller in deterioration of the critical current value as compared with a coil molded after completion of an oxide superconducting wire. Deterioration of the critical current value can be effectively suppressed by employing the wind and react technique particularly in preparation of a coil of an oxide superconducting wire having a diameter of not more than 100 mm.

On the other hand, the wind and react technique has such a disadvantage that the completed coil of the oxide superconducting wire is unusable if the wire is blistered in the second heat treatment (step S6). Therefore, the wind and react technique is not frequently employed for manufacturing a coil of an oxide superconducting wire in practice.

When the inventive heat treatment method is applied in the second heat treatment (step S6), however, a coil of an oxide superconducting wire can be prepared through the wind and react technique while suppressing blisters of the wire. Thus, deterioration of the critical current value can be effectively suppressed in the case of molding the wire into a coil. The remaining method of manufacturing an oxide superconducting wire is identical to the method of manufacturing an oxide superconducting wire according to the first embodiment shown in Fig. 2, and hence redundant description is not repeated.

(Eighth Embodiment)

The first embodiment has been described with reference to the case of gently increasing the pressure in the atmosphere from the atmospheric pressure according to the state equation of gas before starting the pressurization in the heat treatment (A in Fig. 11), as shown in Fig. 11. However, the inventors have found that the number of blisters formed on the wire can be further reduced by holding the wire under a decompressed atmosphere before starting the pressurization in the heat treatment (A in

Fig. 11). The reason for this is now described.

As described with reference to the first embodiment, the gas in the atmosphere penetrates into the wire through pinholes when the pressure in the atmosphere exceeds the pressure in the wire. Therefore, the wire is held under a decompressed atmosphere before the pressurization in the heat treatment is started, so that the pressure in the atmosphere does not exceed the pressure in the wire. Thus, gas hardly penetrates into the wire also in the state before the pressurization in the heat treatment is started, and formation of blisters on the wire can be further suppressed.

The inventors have investigated the effect of holding the wire under a decompressed atmosphere before the pressurization in the heat treatment is started. More specifically, they prepared oxide superconducting wires while setting pressures to about 0.1 MPa (atmospheric pressure) and 10 Pa respectively before starting pressurization in heat treatments. These oxide superconducting wires were dipped in a vessel charged with liquid nitrogen pressurized to 1 MPa, and left for 24 hours. Thereafter the numbers of blisters formed on the respective oxide superconducting wires were examined. Consequently, the oxide superconducting wire prepared by setting the pressure to about 0.1 MPa (atmospheric pressure) before starting the pressurization in the heat treatment caused a blister per 1000 m. On the other hand, the oxide superconducting wire prepared by setting the pressure to about 10 Pa before starting the pressurization in the heat treatment exhibited absolutely no blisters. Thus, it is understood that blisters of the oxide superconducting wire can be further suppressed by holding the wire under a decompressed atmosphere before the pressurization in the heat treatment is started.

This embodiment has been described with reference to the case of holding the wire under a decompressed atmosphere before the pressurization in the heat treatment is started, as a method of manufacturing an oxide superconducting wire. In place of this case, however, the present invention is also applicable as a heat treatment step carried out on a manufactured oxide superconducting wire, i.e., a method of modifying an oxide

superconducting wire. Also when the inventive heat treatment is applied as a method of modifying an oxide superconducting wire, the critical current density of the oxide superconducting wire can be improved.

- 5 The embodiments disclosed in the above must be considered illustrative in all points and not restrictive. The range of the present invention is shown not by the aforementioned embodiments but by the scope of claim for patent, and intended to include all corrections and modifications within the meaning and range equivalent to the scope of claim for patent.